

# PATENT SPECIFICATION

1,156,099

DRAWINGS ATTACHED.

Inventors:—DAVID GRAHAM SHIPLEY and NOEL WATCHORN.

1,156,099



Date of filing Complete Specification: 29 May, 1968.

Application Date: 3 July, 1967. No. 30575/67.

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Index at Acceptance:—C2 C(KC20Y, KC29Y, KC29X, KC30Y, KC34Y, KC341, KC480, KC578, KC626, KD20Y, KD30Y, KD34Y, KD341, KD578, KD626, KD636, KD727); C1 A(F1U, F6).

Int. Cl.:—C 07 c 127/00; C 07 d 55/36.

## ERRATUM

SPECIFICATION NO. 1,156,099

Page 1, for Index at Acceptance C2C only read:—

(20Y, 29Y, 29X, 30Y, 34Y, 341, 480, 578, 626, 636, 727, KC, KD).

THE PATENT OFFICE,  
22nd January 1970

D 121682/2

the particularly essential part of the following statement:—

- 10 This invention relates to the pyrolysis of urea, and to the production and separation of its autocondensation products, in particular biuret, therefrom. The production of such autocondensation products, in particular biuret, is commonly carried out by heating
- 15 urea in a reactor, or series of reactors, at temperatures between 130°C and 210°C, so as to form biuret with the evolution of ammonia. This reaction proceeds more rapidly at higher temperatures, but as the biuret is formed it reacts with the hitherto-unreacted urea to form triuret and cyanuric acid. It is customary, therefore, to draw off the molten mass (consisting of urea, biuret,
- 20 triuret and cyanuric acid) from the reactor(s) when its biuret, triuret and cyanuric acid contents are at a favourable level, and to separate these three components, as far as possible, from the unreacted urea which is recycled to the reactor(s).
- 30 The standard method of separation is to dissolve the molten mixture in water, cool to crystallise the biuret, triuret and cyanuric acid (which are less soluble than urea), filter out the biuret, triuret and cyanuric acid, reduce the water content of the urea filtrate by evaporation, and recycle it to the reactor(s). The main faults of this method are:—
- 35 (i) Not all the biuret can be crystallised

uric acid.

- (ii) Some urea is lost by hydrolysis during the evaporation step.

We have now found that these disadvantages can be overcome by the present invention which provides a process for the separation of urea from a mixture of urea and its auto-condensation products, in particular biuret, triuret and cyanuric acid, which comprises the steps of dissolving said mixture in water, treating the solution with a complexing agent adapted, at the temperature of the solution, to form with the urea an insoluble complex which can be decomposed back into urea and complexing agent by subsequent heating, and separating said insoluble complex from the solution in which said auto-condensation products remain dissolved. After the insoluble complex has been separated therefrom, the auto-condensation products can be crystallised out of the solution by methods known *per se*. The separated insoluble complex is preferably decomposed back into urea and complexing agent by subsequent heating.

Of the compounds which are known to form insoluble complexes with urea which can be decomposed back into urea and complexing agent by subsequent heating, we prefer to use saturated straight-chain hydrocarbons or hydrocarbon derivatives. Using such hydro-

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## COMPLETE SPECIFICATION.

### Improvements in and relating to the Production of Auto-Condensation Products of Urea, in Particular Biuret.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, Millbank, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the pyrolysis of urea, and to the production and separation of its autocondensation products, in particular biuret, therefrom. The production of such autocondensation products, in particular biuret, is commonly carried out by heating urea in a reactor, or series of reactors, at temperatures between 130°C and 210°C, so as to form biuret with the evolution of ammonia. This reaction proceeds more rapidly at higher temperatures, but as the biuret is formed it reacts with the hitherto-unreacted urea to form triuret and cyanuric acid. It is customary, therefore, to draw off the molten mass (consisting of urea, biuret, triuret and cyanuric acid) from the reactor(s) when its biuret, triuret and cyanuric acid contents are at a favourable level, and to separate these three components, as far as possible, from the unreacted urea which is recycled to the reactor(s).

The standard method of separation is to dissolve the molten mixture in water, cool to crystallise the biuret, triuret and cyanuric acid (which are less soluble than urea), filter out the biuret, triuret and cyanuric acid, reduce the water content of the urea filtrate by evaporation, and recycle it to the reactor(s). The main faults of this method are:—

(i) Not all the biuret can be crystallised

out by cooling. For example, about 30% of the biuret leaving the reactor(s) may be returned thereto with the urea filtrate, and the presence of this substantial amount of biuret in the recycle liquor encourages the formation of greater quantities of triuret and cyanuric acid.

(ii) Some urea is lost by hydrolysis during the evaporation step.

We have now found that these disadvantages can be overcome by the present invention which provides a process for the separation of urea from a mixture of urea and its auto-condensation products, in particular biuret, triuret and cyanuric acid, which comprises the steps of dissolving said mixture in water, treating the solution with a complexing agent adapted, at the temperature of the solution, to form with the urea an insoluble complex which can be decomposed back into urea and complexing agent by subsequent heating, and separating said insoluble complex from the solution in which said auto-condensation products remain dissolved. After the insoluble complex has been separated therefrom, the auto-condensation products can be crystallised out of the solution by methods known *per se*. The separated insoluble complex is preferably decomposed back into urea and complexing agent by subsequent heating.

Of the compounds which are known to form insoluble complexes with urea which can be decomposed back into urea and complexing agent by subsequent heating, we prefer to use saturated straight-chain hydrocarbons or hydrocarbon derivatives. Using such hydro-

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carbon or hydrocarbon derivatives, the stability of the complex increases with increasing molecular weight and decreases with increasing temperature. If, therefore, the separation of the urea is to be effected at high temperatures (say, above 50°C or 60°C) it is advisable to use a complexing agent of high molecular weight which will, in any case, increase the efficiency of the separation.

The invention further provides a process for the production of autocondensation products of urea, in particular biuret, triuret and cyanuric acid, by the pyrolysis of urea in one or more reactors, which comprises the steps of drawing off the molten mixture (comprising urea, biuret, triuret and cyanuric acid) from the reactor(s), dissolving said mixture in water, adding to the solution a complexing agent adapted to form with the dissolved in urea an insoluble complex which precipitates out and which can be decomposed back into urea and complexing agent by subsequent heating, separating said insoluble complex from the solution, and crystallising out said autocondensation products (in particular biuret, triuret and cyanuric acid) from the solution. The separated insoluble complex is preferably recycled to the process.

One embodiment of the invention is illustrated in Fig. 1 of the accompanying drawings. Urea is pyrolysed in a reactor or series of reactors 1 to form a molten mixture of urea and its auto-condensation products (mainly biuret, with some triuret and cyanuric acid). The molten mixture is drawn off into a solution and complexing tank 2 wherein the mixture is dissolved in water and a complexing agent (e.g. a paraffin) added to form, with the urea, an insoluble complex which precipitates out. (There may, conveniently be two separate tanks, one for solution and another for complexing, instead of the combined tank 2 illustrated). The insoluble complex and the solution are passed to a centrifuge 3 where they are separated, the insoluble complex being passed to a decomposer 4 where it is decomposed by heat into urea and complexing agent. These are separated, the urea being recycled to the reactor(s) 1 and the complexing agent to the solution and complexing tank 2. (In fact, the decomposer 4 is not essential; the insoluble complex may be recycled directly to the reactor(s) 1 where the temperature is sufficiently high to effect the decomposition, the complexing agent is allowed to remain in the reactor(s) 1, and as the molten mixture containing complexing agent is drawn off into the solution and complexing tank 2, the complexing agent re-combines with the urea to form the insoluble complex). As illustrated, fresh urea is added to the insoluble complex before it is passed to the decomposer 4, but obviously such fresh urea could equally well be supplied directly to the reactor(s) 1.

The solution from the centrifuge 3 is passed to a crystalliser 5 where the dissolved biuret (and other auto-condensation products) are crystallised out, and thence to centrifuge 6 where they are separated from the solution, dried in a drier 7 and recovered. The remaining solution, which still contains some biuret and other auto-condensation products and possibly some urea, is recycled from centrifuge 6 to the solution and complexing tank 2.

It is evident, from the above, that only urea (with complexing agent) is recycled to the decomposer 4 and reactor(s) 1; no biuret is recycled thereto, and there is consequently a reduction in the amount of triuret and cyanuric acid formed therein. Furthermore, the urea complex is returned to the decomposer 4 in solid form, thereby eliminating the costly and troublesome evaporation step of the known separation methods and the loss of urea by hydrolysis which this involves.

The invention further provides a process for the production of autocondensation products of urea, in particular biuret, triuret and cyanuric acid, by the pyrolysis of urea in one or more reactors, which comprises the steps of drawing off the molten mixture (comprising urea, biuret, triuret and cyanuric acid) from the reactor(s), dissolving said mixture in water, crystallising out and separating the auto-condensation products (comprising biuret, triuret and cyanuric acid) from the solution, adding to the separated urea-containing solution a complexing agent adapted to form with the dissolved urea an insoluble complex which precipitates out and which can be decomposed back into urea and complexing agent by subsequent heating, separating said insoluble complex from the solution, decomposing the separated insoluble complex back into urea and complexing agent by heating, and recycling the urea to the reactor(s) and the complexing agent to the complexing step.

A further embodiment of the invention is illustrated in Fig. 2 of the accompanying drawings. As in the case of Fig. 1, the molten mixture (comprising urea, biuret, triuret and cyanuric acid) is drawn off from the reactor(s) 1 and dissolved in water in a dissolving tank 8. The resulting solution is treated in a crystalliser 9 to crystallise out the auto-condensation products (biuret, triuret and cyanuric acid) which are separated out in centrifuge 10, dried in a drier 11 and recovered. The separated urea-containing solution is passed to a complexing tank 12 to which there is added a complexing agent adapted to form, with the urea, an insoluble complex which precipitates out and is separated in centrifuge 13. The separated solution (which still contains some biuret, triuret and cyanuric acid, and possibly some urea) is recycled to the dissolving tank 8, while the separated insoluble complex is passed to a decomposer 14 where, by the

action of heat, it is decomposed and separated back into urea and complexing agent. The separated urea is recycled to the reactor(s) 1 and the separated complexing agent is recycled to the complexing tank 12. As illustrated, fresh urea is added to the complex before the latter is passed to the decomposer 14, but obviously such fresh urea could equally well be fed directly to the reactor(s) 1.

As in the case of Fig. 1, no biuret (or other auto-condensation products) are recycled to the reactor(s) 1. Any biuret not crystallised out and separated by centrifuge 10 is removed from centrifuge 13 and recycled to the dissolving tank 8, thereby by-passing the reactor(s) 1, and reducing the amount of triuret and cyanuric acid formed therein. Furthermore, the urea complex is returned to the decomposer 14 in solid form, thereby eliminating the costly and troublesome evaporation step of the known separation methods and the loss of urea by hydrolysis which this involves.

#### WHAT WE CLAIM IS:—

1. Process for the separation of urea from a mixture of urea and its auto-condensation products, in particular biuret, triuret and cyanuric acid, which comprises the steps of dissolving said mixture in water, treating the solution with a complexing agent adapted, at the temperature of the solution, to form with the urea an insoluble complex which can be decomposed back into urea and complexing agent by subsequent heating, and separating said insoluble complex from the solution in which said auto-condensation products remain dissolved.

2. Process as claimed in Claim 1, wherein the autocondensation products are crystallised out of the solution after the insoluble complex has been separated therefrom.

3. Process as claimed in Claim 1 or Claim 2, wherein the separated insoluble complex is decomposed back into urea and complexing agent by heating.

4. Process for the production of auto-condensation products of urea, in particular biuret, triuret and cyanuric acid, by the pyrolysis of urea in one or more reactors, which comprises the steps of drawing off the molten mixture (comprising urea, biuret, triuret and cyanuric acid) from the reactor(s), dissolving said mixture in water, adding to the solution a complexing agent adapted to form with the dissolved urea an insoluble complex which precipitates out and which can be de-

composed back into urea and complexing agent by subsequent heating, separating said insoluble complex from the solution, and crystallising out said autocondensation products (in particular biuret, triuret and cyanuric acid) from the solution.

5. Process as claimed in Claim 4, wherein the separated insoluble complex is decomposed back into urea and complexing agent by heating and recycled to the process.

6. Process for the production of auto-condensation products of urea, in particular biuret, triuret and cyanuric acid by the pyrolysis of urea in one or more reactors, which comprises the steps of drawing off the molten mixture (comprising urea, biuret, triuret and cyanuric acid) from the reactor(s), dissolving said mixture in water, crystallising out and separating the autocondensation products (comprising biuret, triuret and cyanuric acid) from the solution, adding to the separated urea-containing solution a complexing agent adapted to form with the dissolved urea an insoluble complex which precipitates out and which can be decomposed back into urea and complexing agent by subsequent heating, separating said insoluble complex from the solution, decomposing the separated insoluble complex back into urea and complexing agent by heating, and recycling the urea to the reactor(s) and the complexing agent to the complexing step.

7. Process as claimed in any one of the preceding claims, wherein said complexing agent is a saturated straight-chain hydrocarbon or hydrocarbon derivative.

8. Process as claimed in Claim 7, wherein said complexing agent is a paraffin.

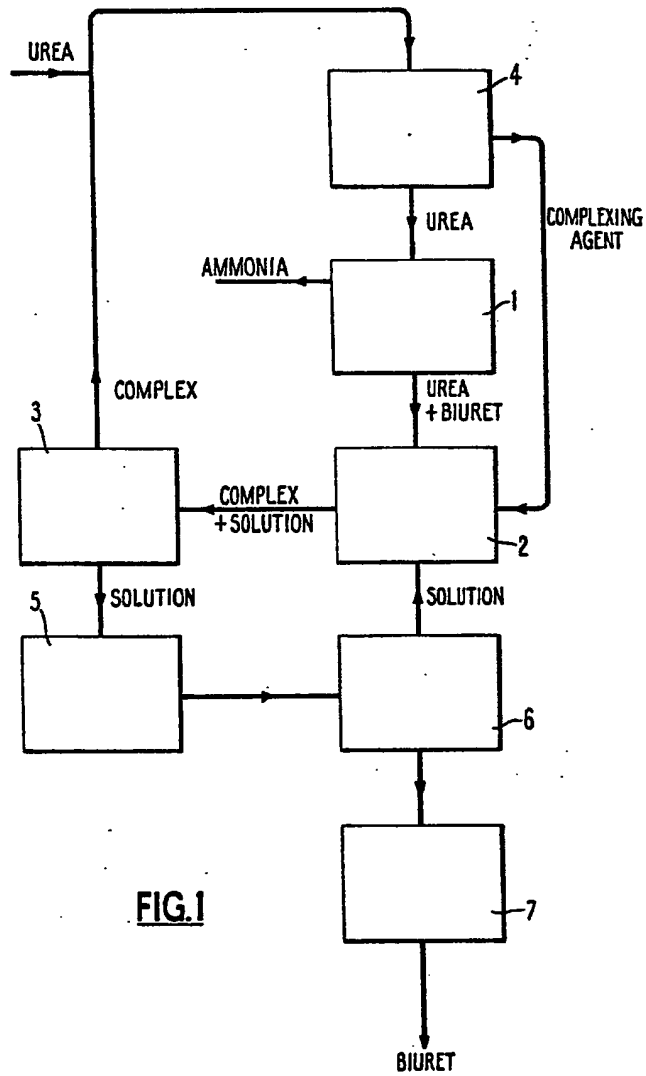
9. Process as claimed in Claim 7 or Claim 8, wherein said complexing agent is of high-molecular weight.

10. Process for the separation of urea from a mixture of urea and its auto-condensation products, substantially as hereinbefore described with reference to the accompanying drawings.

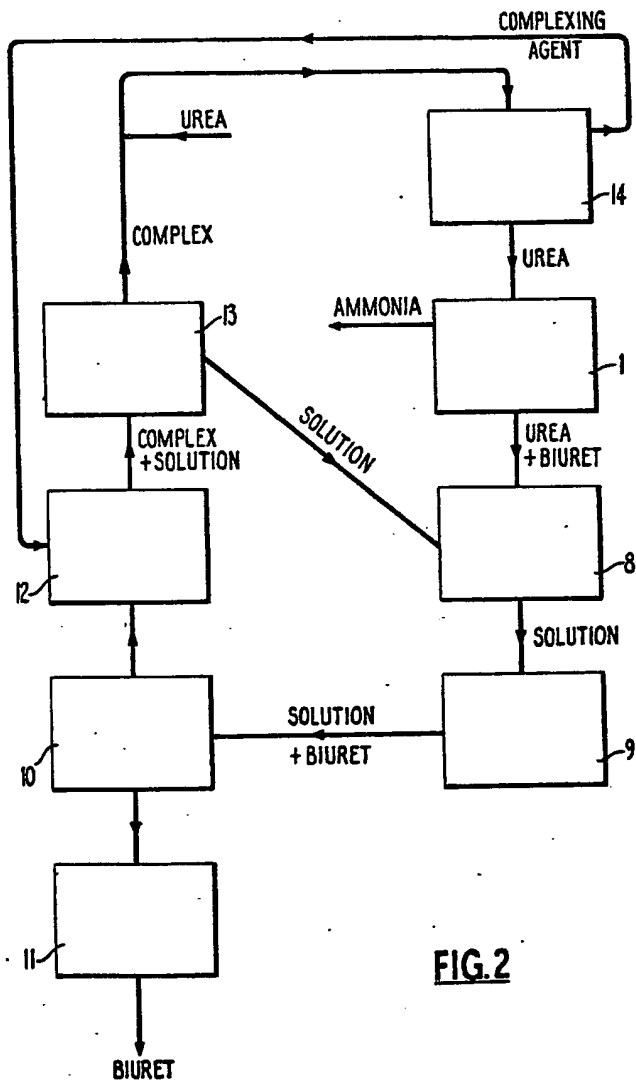
11. Process for the production of auto-condensation products of urea, substantially as hereinbefore described with reference to the accompanying drawings.

12. Autocondensation products of urea whenever obtained by a process substantially as hereinbefore described with reference to the accompanying drawings.

WALTER SCOTT,  
Agent for the Applicants.



**FIG.1**



**FIG. 2**